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(54) METALLISED BODIES

(71) We, **AKADAMIE DER WISSENSCHAFTEN DER DDR**, of 5, Rudower Chaussee, 1199 Berlin, German Democratic Republic, a Corporation organised under the laws of the German Democratic Republic, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with metallised bodies in the form of plates, films strips and profiles comprising thermoplastic polymeric materials, such as polyethylene terephthalate, polymethacrylate, polyurethane, polyamide, polyolefin or polycarbonate, or thermostable polymeric materials, such as polyquinoxaline, a polymeric adhesive layer and a metallic covering layer with an improved adhesion of the metallic covering layer on to the polymeric material, and is also concerned with a process for the production of these metallised bodies.

It is known to coat polymeric materials by vapour deposition in a vacuum or by reductive deposition from metal salt solutions, for which purpose multi-stage processes are generally necessary, to provide a metallic covering layer which imparts to the polymeric materials new properties, such as a high surface conductivity, light impermeability, heat radiation reflectivity, surface hardness and a metallic appearance.

The useful properties of these polymer-metal composites are dependent not only upon the properties of the individual components but also upon the adhesion of the metallic covering layer on to the polymeric material. For the improvement of the adhesion, the surface of the polymeric materials can either be roughened by known physical processes, for example sand blasting, or can be prepared by a chemical treatment in such a manner that a substantially mechanical anchoring of the metal on the polymer material is made possible, similarly to the so-called "press-button" mechanism described in the case of ABS polymers (see W. Riedel, *Galvanotechnik* 57, 579—583/1966).

For the chemical production of hollow spaces by etching, components of the polymeric materials are dissolved out from the surface thereof by the action of organic solvents, for example, acetone, or of acids, for example, sulphuric acid, hydrochloric acid, trichloroacetic acid or chromosulphuric acid, and/or of alkaline agents, for example aqueous or alcoholic solutions of sodium hydroxide or alkaline hydrazine hydrate solution. According to another known process, the polymeric material is treated with a dissolved metal salt complex in the presence of a solvent which can wholly or partially dissolve or swell the polymer.

The etching process in question is then followed by a sensitisation of the polymeric material, preferably with stannous chloride, and subsequently an activation thereof by the action of solutions of noble metal salts, for example, by the use of palladium chloride or of silver nitrate, ionogenic or colloidal form. Materials prepared in this manner can then be provided electrolytically with the desired metallic covering layer and can possibly be further coated.

A particular disadvantage of all the above-mentioned known etching processes is that, with the process for the dissolving out of individual components from the surface of the polymeric material, its mechanical properties, especially in the case of a large surface/volume ratio, for example in the case of films or strips, are impaired to such an extent that these methods are of questionable utility for large-scale use. Furthermore, it is desirable to improve the adhesive strength of the metallic covering layer to the polymeric carrier material: according to the above-described known methods, the adhesive strength obtained is only about 100 p/6.5 mm.

For the improvement of the adhesive strength of the metal to the polymer material, a number of other processes use binding agents or adhesives, for example mixed polymers of acrylamide/methacrylamide and polyvinyl butyrate or of vinylidene chloride and acrylonitrile or a polyester of

ethylene glycol, terephthalic acid and isophthalic acid or a polyurethane from a urethane pre-polymer based on polyester and a polyisocyanate, which are applied to the carrier material or substrate by dipping or spraying in the form of dispersions or solutions. Before application, these binding agent layers are either mixed with finely powdered metals, for example aluminium, copper or silver, or, after application, such finely powdered metals are sprayed on to the still moist surface or colloidal metals, for example palladium, are deposited by reductive treatment from solutions of noble metal salts. This metal deposition permits not only a subsequent metallisation of the polymeric material by electrolytic means but also the current-free deposition of further metallic material in a metallising bath on to the non-metallic carrier. When using polyurethane bonding layers, which, after drying at 90°C., give, analogously to the other above-mentioned binding agent layers, a compact and transparent film, the metallic coating with, for example, aluminium or silver, is preferably carried out with the use of the vacuum vapour deposition technique.

Polymeric materials of this type coated with metals and having a large surface/volume ratio, such as strips and films, have, in some cases, proved to be very pressure sensitive and, because of insufficient adhesion of the metallic covering layer to the polymeric material, tend to flake off or crack.

The large number of known processes for the improvement of the adhesion of metals on to polymeric materials demonstrates the great importance which is given to this process stage in conjunction with the production of metallised polymeric materials and it clearly seems to be desirable to look for still further improvements in this field, especially with regard to the adhesion of the metallic layer on to the polymeric material.

It is, therefore, an object of the present invention to provide metallised bodies in the form of plates, films, strips and profiles comprising thermoplastic polymeric materials, such as polyethylene terephthalate, polymethacrylate, or polyurethane, polyamide, polyolefin, or polycarbonate, or thermally stable polymeric materials, such as polyquinoxaline, a polymeric adhesive layer and a metallic covering layer with an improved adhesion of the metallic covering layer to the polymeric material, as well as a process for the production thereof by coating one or more sides of a polymeric material to be metallised with a polymeric adhesive layer and subsequent metallisation.

According to the present invention, this problem is solved in that the polymeric adhesive layer is formed between the polymeric substrate and the metallic covering layer as

a poromeric layer, i.e. a microporous layer in which the majority of the micropores present therein are connected to one another by micro-canals, only a small proportion of the micropores being isolated from the rest of the micropores, the micropores and micro-canals being open on the surface of the poromeric layer to which the metallic covering is applied. This poromeric layer is obtainable by coating the bodies to be metallised with a solution and/or dispersion of a polymer which can be coagulated in a moist atmosphere and subsequently coagulating the coating at atmospheric pressure and at a relative atmospheric humidity of more than 40% and preferably of more than 65% to give a poromeric layer. The size and number of the micropores and of the microcanals, as well as the spatial construction of the poromeric layer as a whole, depend upon the temperature and relative atmospheric humidity used for the coagulation.

Examples of polymers which can be used for the formation of the poromeric adhesive layer include, in particular, polyurethane polymers, for example those based on a polyester with a molecular weight of about 2200, diphenylmethane diisocyanate and diaminodiphenylmethane as chain lengthener, as well as linear low molecular weight polyesters based on polyethylene terephthalate, preferably with an average molecular weight of 20,000 to 60,000, and polyvinyl-formal with a molecular weight of about 100,000.

Examples of metals from which the metallic covering layer can be made include zinc, aluminium, copper, chromium, nickel, cobalt, silver and gold.

The process according to the present invention is, in the case of a multi-sided coating, preferably carried out by passing the polymeric material, in a dip process, through a 5 to 20 wt.% solution of the polymeric coating material in dimethyl formamide or in a dimethyl formamide-acetone mixture or through a 5 to 20 wt.% dispersion of the polymeric coating material in a mixture of halogenated hydrocarbons, for example dichloroethane, and dimethylformamide. In the case of a one-sided coating, the above-mentioned dissolved or dispersed polymeric coating material can be poured on to one side of the polymeric material, whereafter the desired layer thickness can be obtained by means of a doctor blade. Another possibility is to paint one side of the polymeric material with the dissolved or dispersed polymeric coating material, whereafter, if necessary, the layer thickness can again be adjusted by means of doctor blade. Subsequently thereto, the coated polymeric material is, for the formation of the poromeric adhesive layer, passed into a drying canal. Air with a relative atmospheric humidity of above 40% and preferably above 65% is

blown into this canal at normal pressure and at a temperature of approximately 30°C. The moisture thus introduced results in a coagulation of the polymeric coating material on the polymeric substrate and, at the same time, brings about the formation of poromeric gel structure which, in the course of a further water-treatment process for the purpose of completely removing the solvent, are fixed at temperatures below 50°C. A subsequent drying of the so prepared material at temperatures above 50°C. provides a polymeric material coated with a poromeric adhesive layer, the surface of which is non-tacky and has a milky-turbid appearance.

Without the use of acidic and/or alkaline etching baths, polymeric material thus provided with a poromeric adhesive layer can be metallised by chemical or vacuum deposition methods using known processes. A subsequent electrolytic strengthening of the metallic covering layer, for example a copper coating, is possible with further copper or with other metals. An addition of gloss-forming agents to the baths provides glossy surfaces.

The adhesive strength of the poromeric adhesive layers produced on the polymeric material by the process according to the present invention, for example on a polyethylene terephthalate material, is, for 6.5 mm., 300 to 400 p. However, even values of approximately 500 p/6.5 mm. can also be obtained.

The adhesive strength of an applied copper layer with a layer thickness of 110 nm is between 300 and 400 p/6.5 mm., the adhesive strength being measured with the use of the method of determination which is conventional for this purpose, i.e. the force needed to pull off a pressed-on adhesive foil.

The adhesive strength of the metal covering layer on the polymeric material achieved by the use of the process according to the present invention is, on average, greater than that which is achieved by the use of the previously known processes. This unexpectedly advantageous result is essentially attributable to the fact that the deposited metal can be practically mechanically anchored into the micropores of the poromeric adhesive layer, somewhat comparably with the above-mentioned "press-button" mechanism in the case of ABS polymers and thus has an adhesion to the polymeric material layer additional to the physico-chemical binding forces. This means that in order to remove the metallic covering layer from the polymeric material, it is necessary not only to overcome the intramolecular forces but also the metal must be freed from its mechanical anchoring in the poromeric adhesive layer.

It is of especial technical importance that

the process according to the present invention permits the omission of the various etching processes which are laborious and considerably reduce the quality of the polymeric material, especially in the case of large surface/volume ratios, for example in the case of strips and films.

By variation of the process parameters, for example, the nature and concentration of the polymeric coating solution, the composition of the solvent mixture, the temperature and the moisture in the air, the microporosity of the poromeric adhesive layer can be varied within wide limits and thus the process of the present invention for metallising polymeric materials is capable of a wide spectrum of technical fields of use, depending upon the desired final properties. A further advantage of the present invention is that the formation of the poromeric adhesive layer can be carried out not only discontinuously, but also continuously, i.e. in the case of a continuous coating, it is possible to produce, for example, endless strips.

The following Examples are given for the purpose of illustrating the present invention;—

EXAMPLE 1.

A 36 μ m. thick polyethylene terephthalate strip is coated on both sides in a dip process with a 10 wt.% solution of a polyurethane in a solvent mixture consisting of 78 wt.% dimethyl formamide and 22 wt.% acetone. The polyurethane is prepared from an adipic acid-diethylene glycol polyester with a molecular weight of 2200 and 4,4'-diisocyanatodiphenylmethane in dimethyl formamide with the formation of a pre-polymer to which, for chain lengthening, diaminodiphenylmethane is added. After the coating, the strip is passed through a drying canal into which is introduced a current of air with a relative atmospheric humidity of 85% and a temperature of 26 to 30°C. For fixing the "partially coagulated" polymeric coating material and thus for the strengthened formation of the poromeric gel structures, the strip is subjected, at a temperature below 50°C., to a further water-treatment process for the complete removal of solvent. Subsequent drying at a temperature above 50°C. provides a non-sticky and opaque polyethylene terephthalate strip coated with a poromeric adhesive layer. The adhesive strength of the poromeric layer on to the carrier material is between 285 and 350 p/6.5 mm.

For metallisation, the strip is sensitised with a stannous chloride solution, activated with an aqueous hydrochloric acid solution of palladium chloride and subsequently subjected to a currentless coppering. The adhesive strength of the copper layer is about 350 p/6.5 mm. at a layer thickness of the copper of 110 nm. Strengthening of the

copper layer is achieved electrolytically, the addition of gloss forming agents to the baths thereby resulting in a smoothed surface.

5 EXAMPLE 2.

In a manner analogous to that described in Example 1, a 36 μ m. thick polyethylene terephthalate strip is coated on both sides with a 20 wt. % solution of a low molecular weight polyethylene terephthalate polyester (M.W. <50,000) in dimethyl formamide/acetone (1:1 by wt.). Coagulation takes place by means of an air current with a temperature of 30°C. and 65% relative atmospheric humidity. After a further water treatment at a temperature of <50°C. for the removal of solvent residues, as well as drying in a current of air at a temperature of >50°C., there is obtained an opaque, poromer-coated carrier strip with a non-sticky surface. The adhesive strength of the poromeric adhesive layer to the polyethylene terephthalate strip is more than 300 p/6.5 mm., i.e. at this value, the stripping off of a pressed-on adhesive foil takes place without a separation of the poromeric layer from the carrier material. The material prepared in this manner can be subjected to a currentless coppering in the manner described in Example 1, without acidic and/or alkaline etching. The adhesion of the copper layer is between 310 and 350 p/6.5 mm. A further electrolytic strengthening of the copper layer with copper or other metals can be carried out.

EXAMPLE 3.

In the manner described in Example 1, a 36 μ m. thick polyethylene terephthalate strip is coated on both sides with a 5 wt. % solution of polyvinyl formal (M.W. ~100,000) in dimethyl formamide. After coagulation thereof with air having a relative humidity of 90%, further water treatment and drying, there is obtained an opaque, non-sticky, poromer-coated carrier strip. The adhesive strength of the poromeric adhering layer on the carrier material is 395 to 500 p/6.5 mm. and a copper layer, applied thereto without the use of current in a manner analogous to that described in Example 1, has an adhesive strength of 320 to 410 p/6.5 mm. It is also possible to carry out a subsequent electrolytic strengthening with a further amount of copper or with another metal.

EXAMPLE 4.

Preparation of a polyurethane dispersion.

140 g. dimethyl formamide are added to 72.3 g. of a 35 wt. % solution consisting of a polyurethane with terminal hydroxyl groups (hydroxyl number 35, molecular weight 3200) and dichloroethane. 7.7 g. of a 75 wt. % solution of a commercially-available urethane pre-polymer (isocyanate equivalent

weight 324) based on toluylene diisocyanate and trimethylolpropane are added to this solution. By the addition of 44 g. of a 30 wt. % solution of a low molecular weight polyethylene terephthalate polyester (hydroxyl number about 5, molecular weight <50,000) in dimethyl formamide, the polyurethane dispersion is formed.

Coating of the carrier material.

A 36 μ m. thick polyethylene terephthalate strip is coated on both sides in a dipping process with a 17 wt. % polyurethane dispersion in a dichloroethane-dimethyl formamide mixture, prepared in the above-described manner. For coagulation, the strip is passed through a canal into which is introduced a current of air with a temperature of 23 to 30°C. and with a relative atmospheric humidity of 50%. After a water treatment of the thus pre-treated strip at a temperature below 50°C. for the removal of all of the solvent and subsequent drying, there is obtained an opaque, poromer-coated polyethylene terephthalate strip with a non-sticky surface. The adhesive strength of the poromeric layer to the carrier material is more than 400 p/9 mm.

For metallisation, the strip is sensitised with a stannous chloride solution, activated with an aqueous hydrochloric acid solution of palladium chloride and subsequently subjected to a current-free coppering. The adhesive strength of the chemically applied copper layer is more than 250 p/9 mm. The copper layer is strengthened electrolytically, the addition of gloss formers to the baths thereby resulting in a smoothed surface.

EXAMPLE 5.

A 3 mm. thick sheet of commercially-available polycarbonate is coated on one side by painting with a 15 wt. % solution of a polyurethane in a solvent mixture consisting of dimethyl formamide and acetone (3:1 by wt.). The polyurethane is prepared in the manner described in Example 1. After coagulation of the polyurethane coating at a temperature of 25 to 30°C. and at a relative atmospheric humidity of 95%, water treatment for the removal of the solvent and drying, there is obtained a non-sticky and opaque polycarbonate sheet coated with a poromeric layer. The adhesive strength of the poromeric layer on to the carrier material is more than 400 p/9 mm., i.e. when stripping off a pressed-on adhesive foil, at 400 p none of the poromeric layer is removed from the carrier material.

Current-free metallising of the sheet is carried out in a manner analogous to that described in Example 1. The adhesive strength of a copper layer is substantially 400 p/9 mm.

EXAMPLE 6.

A 3 mm. thick sheet of commercially-available polymethacrylate is coated, in the manner described in Example 5, with a 15 wt. % solution of a polyurethane by painting on. After coagulation of the polyurethane coating at a temperature of 25 to 30°C. and at a relative atmospheric humidity of 95%, water treatment for the removal of the solvent and drying, there is obtained a non-sticky and opaque polymethacrylate sheet coated with a poromeric layer. The adhesive strength of the poromeric layer on to the carrier material is more than 500 p/9 mm., i.e. when stripping off a pressed-on adhesive foil, at 500 p none of the poromeric layer is removed from the carrier material.

The current-free metallising of the sheet is carried out in a manner analogous to that described in Example 1. The adhesive strength of a copper layer thus applied is substantially 450 p/9 mm.

EXAMPLE 7.

A 3 mm. thick sheet made by the injection moulding of a commercially-available polyurethane is coated on one side, in the manner described in Example 5, with a 15 wt. % solution of a polyurethane by painting on. After coagulation of the polyurethane coating at a temperature of 25 to 30°C. and at a relative atmospheric humidity of 95%, water treatment for the removal of the solvent and drying, there is obtained a non-sticky and opaque polyurethane sheet coated with a poromeric layer. The adhesive strength of the poromeric layer to the carrier material is between 450 and 550 p/9 mm.

The current-free metallising of the sheet is carried out in a manner analogous to that described in Example 1. The adhesive strength of a copper layer thus applied is about 450 p/9 mm.

EXAMPLE 8.

A 100 μ m. thick polyquinoxaline film is coated on one side by painting on, in the manner described in Example 5, using a 15 wt. % solution of a polyurethane. After coagulation of the polyurethane layer at a temperature of 25 to 30°C. and at a relative atmospheric humidity of 95%, water treatment for the removal of the solvent and drying, there is obtained a non-sticky and opaque polyquinoxaline film coated with a poromeric layer. The adhesive strength of the poromeric layer on to the carrier material is more than 500 p/9 mm., i.e. when stripping off a pressed-on adhesive foil, at 500 p none of the poromeric layer is removed from the carrier material.

The current-free metallising of the sheet is carried out in a manner analogous to that described in Example 1. The adhesive

strength of a copper layer thus applied is substantially 450 p/9 mm.

WHAT WE CLAIM IS:—

1. Metallised bodies in the form of sheets, films, strips and profiles, comprising a thermoplastic or thermostable polymeric material, at least one polymeric adhesive layer and a metallic covering layer on said polymeric adhesive layer, the polymeric adhesive layer between the polymeric material and the metallic covering layer being formed as a poromeric layer (as hereinbefore defined).

2. Metallised bodies according to claim 1, wherein the poromeric polymeric adhesion layer is a coagulated polyurethane, polyethylene terephthalate or polyvinyl formal.

3. Metallised bodies according to claim 1 or 2, wherein the thermoplastic polymeric material is a polyethylene terephthalate, polymethacrylate, polyurethane, polyamide, polyolefin or polycarbonate.

4. Metallised bodies according to claim 1 or 2, wherein the thermostable polymeric material is a polyquinoxaline.

5. Metallised bodies according to any of the preceding claims, wherein the metallic covering layer consists of or comprises zinc, aluminium, copper, chromium, nickel, cobalt, silver or gold.

6. Metallised bodies according to claim 1, substantially as hereinbefore described and exemplified.

7. Process for the production of metallised bodies in the form of sheets, films, strips and profiles of thermoplastic polymeric materials with improved adhesive strength of the metallic covering layer on to the polymeric material to be metallised with a polymeric adhesive layer and subsequent metallising, wherein the bodies to be metallised are coated with a solution and/or dispersion of a polymer which can be coagulated in a moist atmosphere and subsequently the coating is coagulated at atmospheric pressure and at a relative atmospheric humidity of more than 40%, to give a poromeric layer, the size and number of the micropores and of the microcanals, as well as the spatial construction of the poromeric layer as a whole depending upon the temperature and relative humidity used for the coagulation.

8. Process according to claim 7, wherein the coagulation is carried out at a relative atmospheric humidity of more than 65%.

9. Process according to claim 7 or 8, wherein a solution of polyurethane, polyethylene terephthalate or polyvinyl formal in dimethyl formamide or dimethyl formamide-acetone is used for the coating.

10. Process according to claim 7 or 8, wherein a dispersion of polyurethane, polyethylene terephthalate or polyvinyl formal in halogenated hydrocarbons and dimethyl formamide is used for the coating.

11. Process according to any of claims 7 to 10, wherein the coated polymeric material, after coagulation, is subjected to a water treatment and drying process for the removal of solvent.
12. Process according to any of claims 7 to 11, wherein at least one metal is deposited discontinuously or continuously by vacuum deposition and/or chemical methods on to the poromeric layer.
13. Process according to claim 7 for the production of metallised bodies, substantially as hereinbefore described and exemplified.
14. Metallised bodies, whenever produced by the process according to any of claims 7 to 13.

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